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Electrooxidation of methanol and 2-propanol mixtures at platinum single crystal electrodes

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ABSTRACT

In the present work the electrooxidation of methanol, 2-propanol and different mixtures of both alcohols has been studied on the three platinum basal planes in three different electrolytes (H_2SO_4, $HClO_4$ and NaOH). The results indicate that, like in the case of both individual alcohols, the electrooxidation of the mixture is a structure sensitive reaction and that Pt(1 1 1) leads to higher current densities for some mixture compositions as compared to what could be expected from the contribution of the individual compounds. The effect of the methanol concentration in the mixture points out that 2-propanol is the main reacting fuel at the Pt(1 1 1) surface. Interestingly, the addition of methanol clearly has a positive effect on 2-propanol oxidation. For a specific mixture composition, while results from cyclic voltammetry indicate a modest twofold increase in current density, chronoamperometric results after 10 min experiment show a nearly 200 times higher current density. IR experiments have been performed to gain information about the enhancement mechanism. Nevertheless, we have found that both methanol and 2-propanol seem to follow the same mechanism as they follow in the absence of the other alcohol, and therefore the enhancement could be probably related to a competitive adsorption for the active surface sites.

1. Introduction

Direct alcohol fuel cells (DAFC) are promising electrochemical power generators especially for portable applications. However, electrooxidation kinetics of alcohols is slow and consequently DAFC power densities are low for practical applications. At present, methanol is one of the most widely studied organic fuels [1–15] and it is known to produce high current densities in DAFC with platinum based catalysts [16]. Nevertheless, during the reaction, the platinum surface becomes poisoned by strongly adsorbed intermediates such as carbon monoxide, due to the dissociative chemisorption of methanol [14,15]. This adsorbed CO, both in linear and bridge-bonded form, has been observed at platinum surfaces [1,14,15]. The reported methanol electrooxidation products are CO_2, HCHO, HCOOH and $HCOOCH_3$ [17,18]. The mechanism of methanol electrooxidation on Pt follows a “dual-pathway” with the additional complication that CO may be also considered as reactive intermediate [18,19]. In addition, methanol electrooxidation on the three basal planes of platinum has been shown to be a structure sensitive reaction [10,18,20]. Among them, Pt(1 1 1) was found to be the least reactive towards methanol decomposition, while Pt(1 1 0) was considered to be the most active. Nevertheless, in a very recent paper, Housmans et al. have investigated the selectivity and structure sensitivity of the methanol oxidation pathways on basal planes and stepped platinum single crystal electrodes by monitoring the mass fractions of CO_2 (m/z 44) and methylformate (m/z 60) using on-line electrochemical mass spectrometry (OLEMS) [21]. They found that methanol oxidation on Pt basal planes showed an increase in maximum activity in the order Pt(1 1 1) < Pt(1 1 0) < Pt(1 0 0). The order obtained is different to that previously reported by Herrero et al. (Pt(1 1 1) < Pt(1 0 0) < Pt(1 1 0)) [10] and it was attributed to differences in the electrode pre-treatment which greatly influences the surface structure of the Pt(1 0 0) and Pt(1 1 0) electrodes. In addition, on the basis of the onset potential of the reaction (<0.6 V), the Pt(1 1 0) was reported to be the most active, followed by the Pt(1 1 1) and Pt(1 0 0) surfaces [21].

Besides the studies with the three basal planes, methanol electrooxidation was also performed on stepped Pt surfaces in order to clarify how exactly the step density influences these reactions. Shin and Korzeniewski suggested that an increase of the step density catalyzes methanol decomposition [22], whereas Tripkovic and Popovic showed that the increase in the step density leads to a decrease in the surface activity towards methanol electrooxidation [23], both using Pt[n(1 1 1) × (1 0 0)] stepped surfaces. In addition, Housmans and Koper studied methanol oxidation on Pt[n(1 1 1) × (1 1 0)] stepped surfaces, and reported an increase in

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the activity with the step density, suggesting that the presence of steps with a (1 1 0) orientation catalyzes methanol decomposition, CO oxidation and also the direct methanol oxidation [24]. These kind of studies are relevant, not only from a fundamental point of view, but also from a practical one, because in practical applications the stepped surfaces may be considered as models of surface defects, always present on dispersed electrodes.

The 2-propanol oxidation has not received as much attention as methanol's. Nevertheless, 2-propanol is an interesting fuel and in comparison with methanol it is less toxic, it has a higher boiling point and it is less prone to crossover through the electrolyte membrane to the cathode side [25,26]. In fuel cell studies, the electrooxidation of 2-propanol over platinum or platinum-containing catalysts supplies, at low current densities, higher voltages than methanol [25]. The products from this oxidation are acetone and carbon dioxide [27,28]. In this way, the number of papers concerning this reaction has greatly grown in the recent years [29–32]. One of the most relevant papers concerning the electrooxidation of 2-propanol on platinum single crystals was published in 1996 by Sun and Lin [28]. Nevertheless, they employed Pt single crystals cooled down in an oxidative atmosphere (air) which is known to introduce surface defects on the electrodes. In a very recent paper, platinum–ruthenium electrodes have been also used for 2-propanol oxidation and rate enhancement has been observed, by not only increasing the current density of the main peak (CV experiments) but also decreasing the onset potential [32]. Finally, and from a more applied point of view, the open circuit potential of 2-propanol is much higher for a 60:40 PtRu catalyst fuel cell than that of methanol providing a broader possible potential area [26]. In summary, it is well established that the nature and the structure of the electrode material play a key role in the adsorption and electrooxidation of both organic fuels.

An interesting alternative to the use of these pure organic fuels may be their combination to form a binary mixture. In a previous paper, Gojkovic et al. [33] studied the electrooxidation of methanol + 2-propanol mixtures, concluding that these mixtures can deliver a significant anodic current over the entire potential range from 0.2 to 0.8 V, which is not observed with pure methanol or pure 2-propanol. Unfortunately, this study was exclusively carried out with polyoriented platinum nanoparticles and consequently the effect of the surface structure could not be evaluated.

The aim of this work is to study the structure sensitivity of this methanol + 2-propanol binary fuel oxidation on platinum. To our knowledge no work has been focused on the effect of the surface structure in this type of alcohol mixtures. In this way, this paper describes the first results concerning the electrooxidation of alcohol mixtures in platinum single crystals. The interest is focused on finding synergetic conditions in which the reactivity of the mixture could be higher than that expected from the individual contributions. This would lead to electrocatalytic effects on heterogeneous surfaces from changes in the solution composition.

2. Experimental

Platinum single crystals were oriented, cut, and polished from small single crystal beads (2.5 mm diameter) by the procedure described previously [34]. The electrodes were flame-annealed, cooled down in a H_2 + Ar atmosphere and protected with water in equilibrium with this gaseous mixture in the usual way [35]. It has been shown that this treatment leads to well-defined surfaces [36]. A single crystal platinum bead, obtained by melting and slowly cooling a Pt wire, was used as a well-defined polycrystalline surface having a uniform distribution of all surface sites.

Electrochemical experiments were carried out in two conventional three-electrode cells using large Pt counter electrodes. The potentials were measured against a reversible hydrogen electrode (RHE) connected to the cell through a Luggin capillary. One cell was filled with the electrolyte in the absence of alcohol or alcohol mixture under study. The second cell contained the alcohol, or alcohol mixture, at controlled concentration. Solutions were prepared by the addition of 2-propanol and/or methanol to 0.1 M $HClO_4$, 0.5 M H_2SO_4 or 0.5 M NaOH. All reagents were of p.a. quality (Merck). Solutions were prepared using Millipore Milli-Q water. Oxygen was eliminated by bubbling Ar (Air Liquide N50) for 20 min. The Ar atmosphere was maintained inside the cell during the experiments. To keep a constant concentration of the alcohols in solution, the Ar was previously bubbled through a solution of the same composition as the one in the electrochemical cell. Before any experiment was started, the potential was always kept at 0.05 V. The electrode potential was controlled using a PGSTAT30 AUTOLAB system.

Initial cyclic voltammograms recorded at 50 mV s^{-1} were always performed in the cell without the alcohol or alcohol mixture in order to check the surface structure of the electrode after flame annealing. Subsequently, the electrode was transferred to the second cell with the solution under study where the sweep rate used was 20 mV s^{-1}. Before the chronoamperometric measurements, the electrode was removed from the second cell, washed carefully with ultrapure water to remove possible CO residues and placed back in the second cell at 0.05 V. The chronoamperometric measurements were performed at 0.5 V vs. RHE for 600 s.

Spectroelectrochemical experiments were carried out with a Nicolet Magna 850 spectrometer equipped with a narrow-band DC-coupled MCT-A detector. The spectroelectrochemical cell was provided with a prismatic CaF_2 window bevelled at 60°. A reversible hydrogen electrode (RHE) and a platinum foil were used as reference and counter electrodes, respectively. Unless otherwise stated,

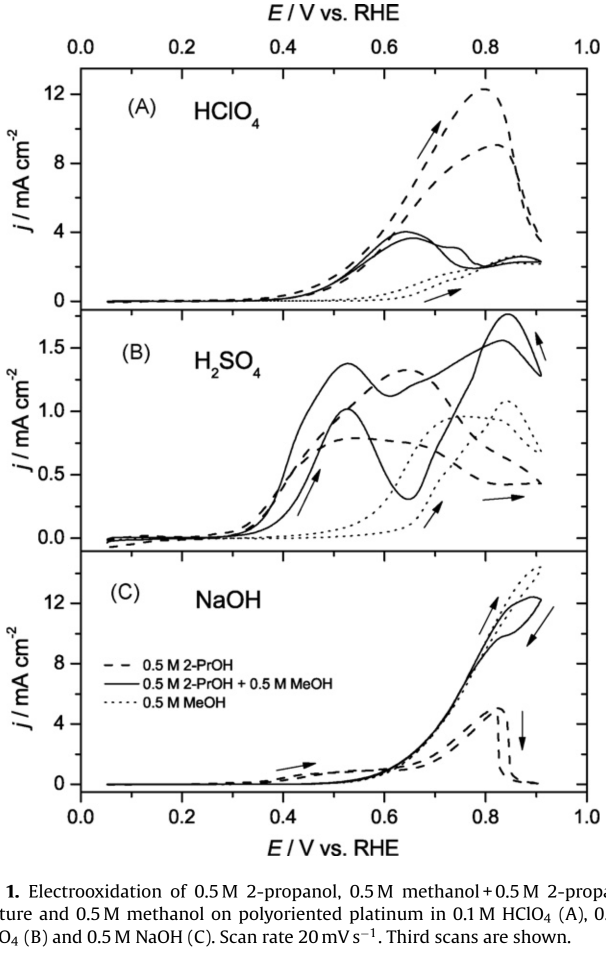

Fig. 1. Electrooxidation of 0.5 M 2-propanol, 0.5 M methanol + 0.5 M 2-propanol mixture and 0.5 M methanol on polyoriented platinum in 0.1 M $HClO_4$ (A), 0.5 M H_2SO_4 (B) and 0.5 M NaOH (C). Scan rate 20 mV s^{-1}. Third scans are shown.